

Polychlorinated Biphenyls

in BASF Batch Wastewater Discharge to New Castle County Sewer



Rick Greene



DE DNREC, Watershed Assessment

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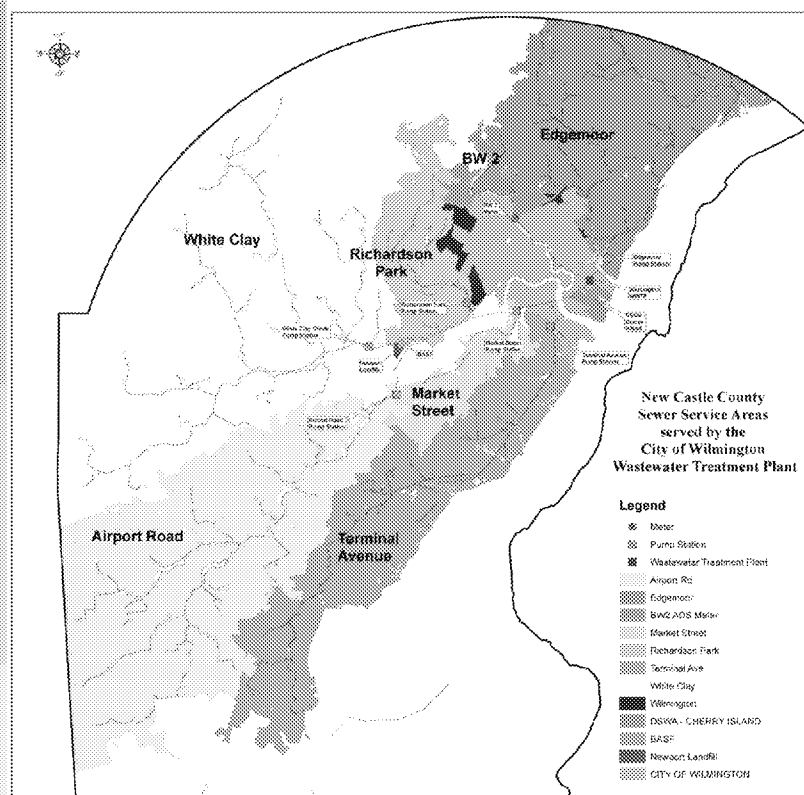
Background

- City of Wilm has an NPDES permit to discharge treated wastewater to the Delaware Estuary.
- PCB discharge from the City's WWTP exceeds wasteload allocation established by EPA as part of the Total Maximum Daily Load (TMDL) for PCBs in the Delaware Estuary.
- The City's NPDES permit contains a special condition to reduce PCB mass loading to Estuary through a Pollutant Minimization Plan (PMP).
- Key element of the PMP is a PCB "trackback" study.

Trackback Study Components




- Map the “sewershed” to delineate service areas. 
- Collect 24-hr composite samples at major pump stations, selected pre-treatment discharges (*including BASF*), plus influent/effluent of City’s WWTP under 3 wet & 3 dry periods (*2 dry & 1 wet events collected thus far*). Also record flows.
- Analyze samples for PCB congeners using method 1668A & verify data meet method performance criteria.
- Summarize PCB concentrations & mass loads (*compare totals & fingerprints; perform flow & mass balances; prioritize sources & source areas*). 

NCC & Wilmington Sewershed Map

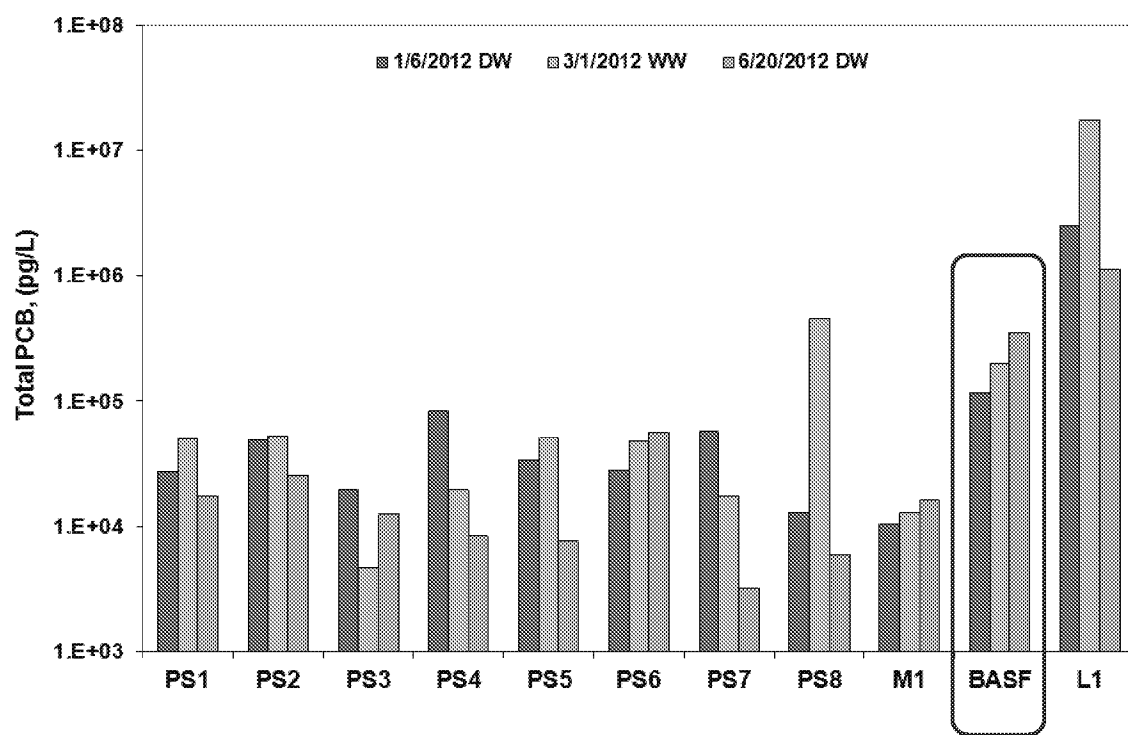


BASF Total PCB & Flows

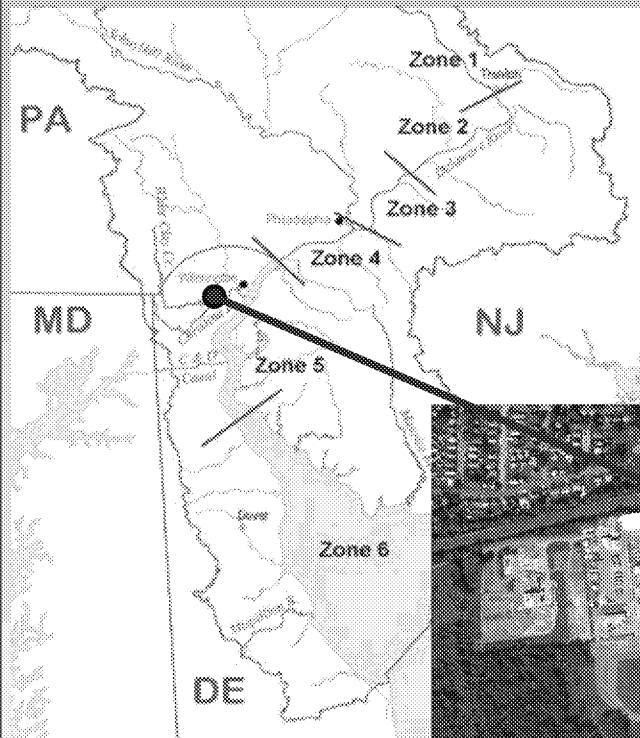
Date	Weather	[PCB] (pg/L)	Flow (MGD)	Mass Load (mg/d)	Percent of Total Load
1/5/2012	dry	114,968	0.747	325	2.3
3/1/2012	wet	197,195	0.8382	626	2.0
6/26/2012	dry	344,968	0.3512	458	9.3

- PCBs detected in all 3 samples so far.
- Concentrations among highest of all samples, even though % contribution to total mass load is low to moderate. 
- For comparison, the PCB TMDL for Zone 5 of Delaware Estuary is 48 mg/d and the WLA portion is 15.6 mg/d (EPA, 2003). 
- IMPORTANTLY, even if Wilm WWTP removes 85% of influent load, the load from BASF is enough, by itself, to exceed TMDL & Σ WLA. 

Total PCB for BASF vs Other Samples



Delaware Estuary Zones

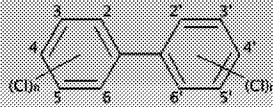


- Zone 5 falls between the PA/NJ/DE line to Liston Point, DE and includes the tidal Christina R.
- BASF lies along the tidal Christina in Newport, DE.
- BASF wastewater is discharged to the Christina River force main, which flows to the City of Wilm's WWTP.

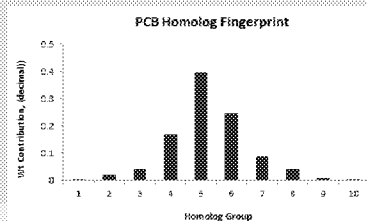
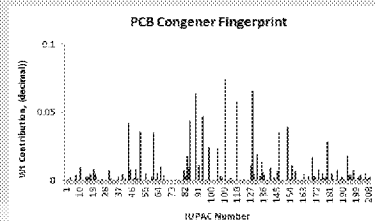


PCB Terminology & Fingerprinting

- *Congener*: refers to a unique chlorine substitution pattern. 209 possible.



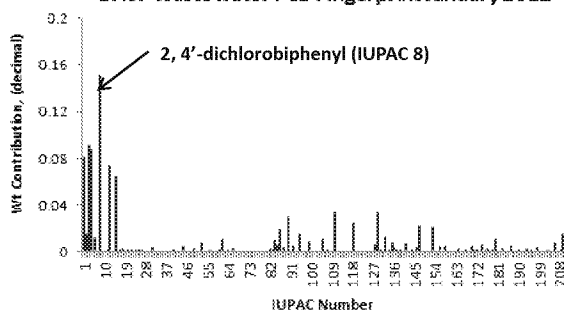
- *Homolog*: refers to all congeners with the same number of chlorines, regardless of positioning. 10 homolog groups possible.
- *Total PCB* = sum of 209 congeners or sum of 10 homologs
- *Fingerprint*: is the array of mass fractions produced by dividing the individual congener or homolog concentrations by total PCB.



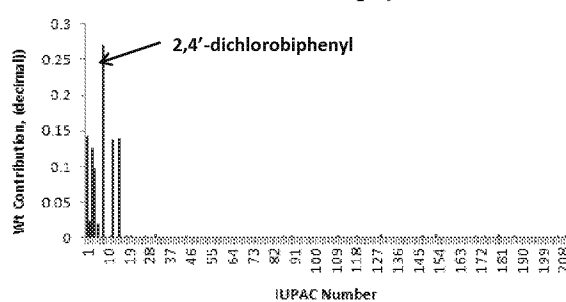
- Common *Arochlor* fingerprints are dominated by tetra through hepta congeners or homologs (Rushneck et.al., 2004). ***Deviations raise flags.***

BASF Wastewater PCB Fingerprint

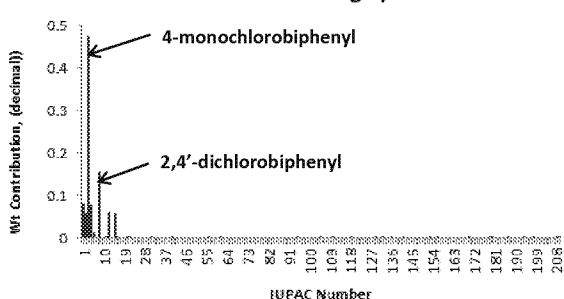
BASF Wastewater PCB Fingerprint January 2012



BASF Wastewater PCB Fingerprint March 2012



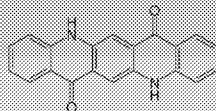
BASF Wastewater PCB Fingerprint Jun 2012



- All 3 samples dominated by the same 9 mono & dichlorobiphenyls.
- No resemblance to common commercial PCB mixtures (Aroclors)
- BASF pattern resembles commercial paint pigment (ES&T, 44, 2822-2827)

Inadvertent Production?

- BASF Newport manufactures Quinacridone pigment (QA).



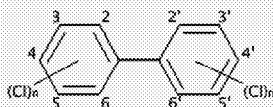
- Therminol VP-1 is used in QA synthesis. It contains ~26.5% Biphenyl, the basic building block of PCBs.



- Manufacturing process also involves chlorinated anilines (*used as a diazo component*).



- Side-reaction of chloroanilines in the presence of biphenyl may produce PCBs through a free radical mechanism or other means.



Expectations

- Regulatory agencies recognize BASF as a responsible corporate citizen with an interest in environmental protection.
- As such, we expect BASF to investigate, identify and abate the discharge of PCBs entering the sewer.
- We suggest an internal trackdown focusing initially on the QA synthesis process. If inadvertent production confirmed, BASF should consider process modification. If that is not possible, then treatment will be needed.
- BASF's primary P.O.C. for this work will be NCC Special Services with technical assistance from DNREC & DRBC.
- In addition to analysis of wastewater, it is advisable to analyze any major solid waste streams associated with the manufacturing process for PCBs.

References

DRBC. 2005. Rule for Establishing Pollutant Minimization Plan (PMP) Requirements for Point and Non-point Source Dischargers of Toxic Pollutants Following Issuance of a TMDL or Assimilative Capacity Determination (<http://www.state.nj.us/drbc/library/documents/PMPrule-May05.pdf>). Delaware River Basin Commission, West Trenton, NJ.

EPA. 2003. Total Maximum Daily Loads for Polychlorinated Biphenyls (PCBs) for Zones 2-5 of the Tidal Delaware River. Established by U.S. Environmental Protection Agency, Regions II and III, on December 15, 2003.

EPA. 2006. Total Maximum Daily Load for Polychlorinated Biphenyls (PCBs) for Zone 6 of the Delaware River. Established by U.S. Environmental Protection Agency, Regions II and III, on December 14, 2006.

Hu, D., Hornbuckle, KC. 2010. Inadvertent Polychlorinated Biphenyls in Commercial Paint Pigments. Environ. Sci. Technol. 44(8): 2822-2827.

Rushneck, DR, et al. 2004. Concentrations of Dioxin-like PCB Congeners in Unweathered Aroclors by HRGC/HRMS Using EPA Method 1668A. Chemosphere 54: 79-97.

Acknowledgements

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